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MISSOURI UNIV-ROLLA

FEASIBILITY STUDY ON A PROCESS FOR ELECTROLESS METAL DEPOSITION--ETC(U)

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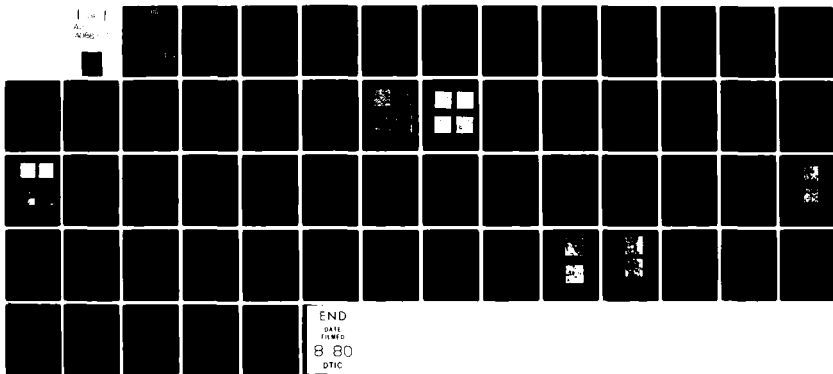
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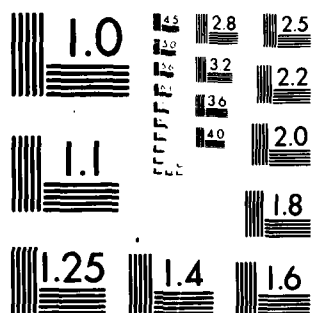
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Annual Report

Feasibility Study on a Process for Electroless Metal Deposition  
In Pits and Fissures of Teeth for Use in Preventive Dentistry

Thomas J. O'Keefe

August 1979

Supported by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Further studies were undertaken to test the feasibility of using metal films, deposited by electroless or chemical means, for use in the military dental program.  The research effort during the past year was concentrated in the following areas: evaluation of the effects of preliminary treatments on the quality of metal plating, the use of alternate or additional etching agents, the testing of alternate reducing agents (other than hydrazine and ferrous sulfate), and morphological and rate studies of the deposited silver films and the effects of additives.					

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## I. INTRODUCTION

Some major advances were made during the past year in improving the properties of the chemically deposited silver layers on tooth-like structure. In addition, the research results helped to establish the degree of importance of many of the operating parameters, such as chemical concentrations, pH, and addition agents.

The major objective of the work was to develop a silver film which rivaled those produced using hydrazine, but by having the reducing reagent be less objectionable, from a toxicity standpoint. Previous animal experiments had shown the use of ferrous sulfate to be less than completely satisfactory. Other non-toxic reducing reagents were evaluated to some degree, but it was found that low concentration additions, such as thiourea, to the  $\text{FeSO}_4$  produced significantly improved silver deposits. In addition, a new technique for enhancing the characteristics of the deposited metal layer was initiated and tested. The process involved electrolytically depositing silver directly onto the electroless silver layer. A new wear test was also developed to allow for a better evaluation of the durability and adherence of the coatings. The advances made in outlining a more substantial and suitable plating system then allowed optimization studies to be conducted. Statistically designed screening tests were used to delineate the effects of process variables and their level on the metal layer produced. This approach gave every indication that it would be very valuable in optimizing the conditions to be used in the plating process.

The results of the work completed during the past year were used as the basis for designing an in vivo animal test conducted in conjunction with USAIDR personnel in the latter part of 1979. Evaluation tests will

be made to determine the level of improvement attained and the areas where additional research or development efforts are needed.

## II. PROCEDURES

### A. Plating

The following sequence of operation was used in electroless plating unless otherwise mentioned: ivory or tooth stored in glycerin, water wash,  $\text{NaHCO}_3$  scrub, water wash, wet polished (ivory only) on 70 micron diamond disc and 600 grit emery paper, 42.5%  $\text{H}_3\text{PO}_4$  etch for 1 minute, water wash, paper blot,  $\text{Ag}^+$  solution (swab 1) -  $\text{Fe}^{+2}$  solution (swab 2) - 30 seconds residence time - reapply  $\text{Ag}^+$  solution from swab 1, wash, repeat for the desired number of applications, wash, and blow dry with  $\text{N}_2$ .

### B. Silver Solutions

Most of the AgF solutions form a black residue, whereas the  $\text{AgNO}_3$  solutions are clear. In order to find out the amount of residue, the AgF solutions were centrifuged and the supernatant liquid was diluted and analyzed for Ag by atomic absorption technique. The results indicate that the residue was about 2-2.5% in 100 gpl solution, whereas it was close to 10% in 1M solution. Thus, the concentrations listed in the report for AgF are probably lower by these percentages due to the precipitated silver.

The technique of measuring the pH of Ag solutions was improved. In the earlier work, litmus paper was used and was prone to some degree of error. The direct use of conventional electrodes viz. calomel and glass electrodes gives very unstable readings due to precipitation of  $\text{AgCl}$  salt in the ceramic porous plug of the calomel electrode. The formation of  $\text{AgCl}$  was avoided by the use of a salt bridge with a reservoir, in which the calomel electrode was immersed. The salt bridge solution was

drained each time a measurement (whether buffer or test solution) was made. The salts used for the bridge solutions were  $\text{NH}_4\text{F}$  or  $\text{KF}$  and  $\text{NH}_4\text{NO}_3$  or  $\text{KNO}_3$  for  $\text{AgF}$  and  $\text{AgNO}_3$  solutions, respectively. The agreement between the pH values measured by paper and meter/salt bridge combination was good in most cases (refer to the first quarterly for 1978-79). These tests also revealed that the pH of Ag solutions changed with time. All pH values of Ag solutions reported here are measured with a pH meter/salt bridge combination. The pH measurements of reducing solutions have been made with a pH meter.

#### C. Wear Tests

One of the important properties of the Ag deposits, besides adherence and appearance, is the resistance to wear. Some preliminary tests were conducted to evaluate the wear resistance of deposits using an electric toothbrush (Broxodent, 3600 strokes/minute). The ivory or tooth was fixed with a doublestick Scotch tape in a shallow container (Petri dish). The dish in turn was fixed similarly to the top of a spring loaded scale (weight interval - one-half oz.) which was placed on a lab-jack. The sample was raised until it touched the toothbrush and a desired weight (1/2 or 1 oz.) was put on the brush. The brushes used were soft, medium, and hard. To simulate the wear conditions that the deposit might be subjected to in practice, a 50 wt % slurry of Crest toothpaste was poured on the sample and the toothbrush was turned on for a predetermined time interval (5 minutes). Then the sample was taken out, washed, blow-dried, and examined under an optical microscope for qualitative evaluation.

The evaluation was not satisfactory due to various factors, such as, non-uniform wear pattern, digging in by the bristles into the substrate

(particularly with ivory), flexing of some bristles on an uneven surface like tooth enamel thereby changing the weight on the brush.

The wear test conditions were improved by using a wheel brush (3/4 inch diameter goat hair soft brush) and a Dremel tool drive. With this type of a set-up, the wear spots were smaller and more uniform. After examining the wear spots under an optical microscope, they were given a number from 0-10, 0 (zero) being the case of a substantial exposure of the substrate and 10 being that of a no visibly detectable damage to or limited penetration into the Ag deposit. A word of caution should be introduced in interpreting the wear numbers in that the numbers are qualitative. The inherent differences in the samples and the experimental variability warrant testing a large number of samples for statistical significance.

The typical speed, weight, and time used for one group of samples were, approximately, 250 rpm (~25 cm/sec surface speed), 14 g, and 30 seconds, respectively. However, if one of the conditions is changed for another group of samples (e.g. 250 rpm, 14 g, and 45 seconds), the wear numbers of the first group cannot be compared directly with those of the second group. The conditions for each group were selected based on the thickness and the type of deposits evaluated in that group. There was one problem, however; the rotational speed of the motor changed sometimes during a test, which was not desirable. This problem was overcome by using a constant speed motor.

### III. ALTERNATE REDUCING AGENT

Another non-toxic reducing agent, ascorbic acid, has been found as a result of screening tests conducted to evaluate potential alternate reducing agents. As the results in Tables I-IV show, the resistance values are quite



low, indicating good coverage on ivory. Table I lists the resistance of the Ag deposit as a function of type of Ag salt and pH. Both  $\text{AgNO}_3$  and AgF work satisfactorily and the pH range is very broad. The results of screening of  $\text{AgNO}_3$  pH and ascorbic acid pH are listed in Table II. The ascorbic acid pH does not appear to be critical whereas there seems to be a preference for higher  $\text{AgNO}_3$  pH for good conductance. The ascorbic acid reduced deposits were evaluated for their wear resistance also, and the results are listed in Table III as a function of the concentration of ascorbic acid. Under the test conditions 150 gpl appears to be optimum with respect to wear resistance. Also the conductance appears to be the best at that concentration. In light of earlier studies with additives it was decided to add thiourea to ascorbic acid and see if the deposit could be further improved. As shown in Table IV, addition of 0.01 gpl thiourea improves the wear as well as conductance.

These results demonstrate that ascorbic acid works well on ivory and deserves further experimentation to see if it would work as well on tooth enamel, particularly because of its non-toxic nature.

#### IV. PREREDUCTION

It was reported earlier that  $\text{Ag}_3\text{PO}_4$  forms after the application of the Ag solution. The nature and quantity of  $\text{Ag}_3\text{PO}_4$  formed could be important from the standpoint of adherence or wear resistance of the film. Table V shows the relative amounts of  $\text{Ag}_3\text{PO}_4$  formed as a function of etching and other treatments.

A portion of the  $\text{Ag}_3\text{PO}_4$  is probably formed by the dissolution of hydroxyapatite with reprecipitation of  $\text{Ag}_3\text{PO}_4$  on the substrate. However,

Table I. Effect of  $\text{AgNO}_3$  or  $\text{AgF}$  pH on the Resistance of Ag Deposit on Ivory. Plating Conditions: 100 gpl  $\text{AgNO}_3$  or  $\text{AgF}$  (pH varying) - 100 gpl ascorbic acid (2.3 pH), 3X, 5X (Ag-Asc. seq.).

Solution	pH	Resistance, $\Omega$	
		3X	5X
$\text{AgNO}_3 + \text{HNO}_3$	1.1	$2 \times 10^4$	120
$\text{AgNO}_3 + \text{HNO}_3$	2.8	15	7
$\text{AgNO}_3$	3.8	90	9
$\text{AgNO}_3 + \text{NH}_4\text{OH}$	6.6	15	4
$\text{AgNO}_3 + \text{NH}_4\text{OH}$	8.0	500	70
$\text{AgNO}_3 + \text{NH}_4\text{OH}$	8.7	24	12
$\text{AgF} + \text{HNO}_3$	0.4	30	2
$\text{AgF} + \text{HNO}_3$	1.7	9	2
$\text{AgF} + \text{HNO}_3$	3.2	8	2
$\text{AgF} + \text{HNO}_3$	5.4	20	5
$\text{AgF}$	6.8	5	2
$\text{AgF} + \text{NH}_4\text{OH}$	7.8	50	12
$\text{AgF} + \text{NH}_4\text{OH}$	8.8	19	8

Table II. Screening of  $\text{AgNO}_3$  pH and Ascorbic Acid pH for Ag Deposition on Ivory. Plating Conditions: 100 gpl  $\text{AgNO}_3$  (pH varying) - 100 gpl ascorbic acid (pH varying), 5X, (Ag-Asc seq.).

Ascorbic Acid pH → $\text{AgNO}_3$ pH	Resistance, $\Omega$			
	No Additive, 2.3	With $\text{NH}_4\text{OH}$		
		3.9	6.9	9.3
2.1 (with $\text{HNO}_3$ )	$8 \times 10^3$	200	10	25
3.8	20	20	50	40
6.9 (with $\text{NH}_4\text{OH}$ )	35	70	17	8
8.0 (with $\text{NH}_4\text{OH}$ )	4	3	2	2

Table III. Resistance and Wear of Ag Deposit on Ivory as a Function of Ascorbic Acid Concentration. Plating Conditions: 100 gpl AgF + HNO<sub>3</sub> (5.1 pH) - x gpl ascorbic acid (~2.3 pH), (Ag-ascorbic acid-Ag seq.), 10X. Wear Conditions: 0.7" dia. goat hair soft wheel brush, 20 cm/sec (208 rpm), 20 g, 30 sec.

Concn. of Ascorbic Acid (gpl)	Resistance ( $\Omega$ )					Wear #
	1X	2X	3X	5X	10X	
50	$>10^7$	$\sim 10^7$	40	4	.16	3
100	$\sim 10^6$	$\sim 10^5$	15	$8-10^3$	.08	4-5
150	$>10^7$	50	$10^2-10^3$	10	.06	6-7
200	12	20	4	1	.40	3
$\sim 330$ (sat.)	$10^2-10^3$	10	10	6	.09	4

Table IV. Resistance and Wear of Ag Deposit on Ivory as a Function of the Concentration of Thiourea Addition to 150 gpl Ascorbic Acid. Plating Conditions: 100 gpl AgF + HNO<sub>3</sub> (5.1 pH) - 150 gpl ascorbic acid + x gpl thiourea (~2.3 pH), Ag-Asc.-Ag seq., 10X. Wear Conditions: 0.7" dia. goat hair soft wheel brush, 20 cm/sec (208 rpm), 20 g, 30 sec.

Concn. of Thiourea (gpl)	Resistance ( $\Omega$ )		Wear #
	5X	10X	
0	10	0.06	6-7
0.01	2.5	0.04	9-10
0.10	60	0.12	5
1.0	0.25	0.10	3

Table V.  $\text{Ag}_3\text{PO}_4/\text{Ca}_5(\text{PO}_4)_3(\text{OH})$  intensity ratio on ivory as a function of surface treatment. Etch, rinse, 100 g/l AgF or  $\text{AgNO}_3$ , 1X. Rinse with water unless otherwise noted. Blow dried. Kept in dark. X-rayed.

$\text{AgNO}_3$ (3.8 pH)	Etch	$I_{\text{Ag}_3\text{PO}_4}/I_{\text{Ca}_5(\text{PO}_4)_3(\text{OH})}$
AgF (3.2 pH)	no etch	1.6
	1M $\text{NH}_4\text{F}$	1.6
	42.5% $\text{H}_3\text{PO}_4$	3.8
	42.5% $\text{H}_3\text{PO}_4^*$	4.5
	42.5% $\text{H}_3\text{PO}_4$	5.3
	42.5% $\text{H}_3\text{PO}_4^*$	4.0

\* Ultrasonic rinse

there could be some direct uptake of Ag into the lattice. The relative coverage of the substrate by  $\text{Ag}_3\text{PO}_4$  was measured by x-ray diffraction. The ratio of the most intense peak of  $\text{Ag}_3\text{PO}_4$  to that of the substrate was taken to be proportional to the coverage. In Table VI, such a ratio is given as a function of the pH of the AgF solution. The coverage is high at low AgF pH's and decreases as the pH increases. This could have further implications on the nature of the final deposit and its properties.

The  $\text{Ag}_3\text{PO}_4$  formed could be changed to Ag by use of a reducing agent, and will be called "prereduction". In a prereduction step, the substrate is prepared in the usual manner, etched,  $\text{Ag}^+$  solution is applied for a fixed time and then washed with distilled water. Following this wash the reducing solution is applied to the surface whereby the  $\text{Ag}_3\text{PO}_4$  is reduced to Ag. The major difference in using prereduction is that the  $\text{Ag}^+$  and reducing solutions are not in contact at the same time. Thus only the condensed  $\text{Ag}_3\text{PO}_4$  or the  $\text{Ag}^+$  dissolved at the interface will be reduced. In prereduction, it is assumed that the bulk of the Ag is reduced from its salt rather than ionically. In Table VII, the degree to which  $\text{Ag}_3\text{PO}_4$  is reduced to Ag is studied as a function of the reducing agent and the number of repetitions. The first repetition for this purpose constitutes only the application of the silver solution. The second and subsequent repetitions constitute washing the sample and applying only the reducing solution. As can be seen from the three ratios shown, for the  $\text{FeSO}_4$  system, the relative amount of  $\text{Ag}_3\text{PO}_4$  decreases and that of Ag increases drastically in the first repetition and then it seems to level off with further repetitions. This indicates that there is still some unreduced  $\text{Ag}_3\text{PO}_4$  on the surface. However, with the ascorbic acid and hydrazine systems, almost all of the  $\text{Ag}_3\text{PO}_4$  is reduced to Ag by the end of two repetitions.

Table VI. Relative coverage of ivory substrate by  $\text{Ag}_3\text{PO}_4$  as a function of AgF pH. (42.5%  $\text{H}_3\text{PO}_4$  etch, ultrasonic rinse 2 min. 100 gpl AgF (+  $\text{HNO}_3$  or  $\text{NH}_4\text{OH}$ ) 30 sec., ultrasonic rinse for 2 min. All tests were done on the same ivory piece.)

AgF pH	$\frac{I_{\text{Ag}_3\text{PO}_4}}{I_{\text{HAP}}}$
0.45	5.2
3.8	2.8
5.3	1.8
7.2	1.2
9.2	0.6



Table VII. Prereduction as a function of reducing agents and number of repetitions. ( $\text{H}_3\text{PO}_4$  etch, wash, 100 g/l AgF +  $\text{HNO}_3$  (pH = 5.3) 30 sec., rinse. Prereduce for X reps.)

Reducing Agent	# of Reps.	$\frac{I_{\text{Ag}_3\text{PO}_4}}{I_{\text{HAP}}}$	$\frac{I_{\text{Ag}}}{I_{\text{HAP}}}$	$\frac{I_{\text{Ag}}}{I_{\text{Ag}_3\text{PO}_4}}$
Saturated $\text{FeSO}_4$ + $\text{H}_2\text{SO}_4$ (pH ~2)	0	1.7	0	0
	1	0.7	2.9	4.3
	2	0.6	2.4	3.8
	3	0.8	2.7	3.6
100 g/l Ascorbic Acid (pH = 2.3)	0	2.0	0	0
	1	0	1.3	--
	2	0	0.6	--
10 ml/l $\text{N}_2\text{H}_4$	0	12.5	0	0
	1	4.1	4.8	1.2
	2	0	7.7	--
	3	0	11.1	--
	4	0	9.1	--

## V. ADDITIVES

In-vivo studies showed that the Ag deposits obtained with  $\text{FeSO}_4$  reductant were less wear resistant than those with hydrazine. Structural and morphological differences between them indicated that a denser more continuous deposit was desirable. Attempts to modify the deposit structure were made by using various additives in reductant solution. The candidates tried were thiourea,  $\text{Na}_2\text{S}_2\text{O}_3$ , NaK tartarate,  $\text{NH}_4\text{CNS}$ , KSb tartarate, and  $\text{Na}_2\text{S}$ . None of these additives except thiourea gave any significant improvement with respect to conductance and wear under the test conditions used; however, they may be effective under different conditions.

The resistance values obtained with thiourea additions are given in Table VIII. Unlike the other additives, thiourea gave deposits with conductivities comparable to or better than those obtained without any additions.

## VI. OPTIMIZATION STUDIES

The presence of thiourea appeared to be promising and hence further tests were undertaken to optimize the various process parameters used in conjunction with the additive.

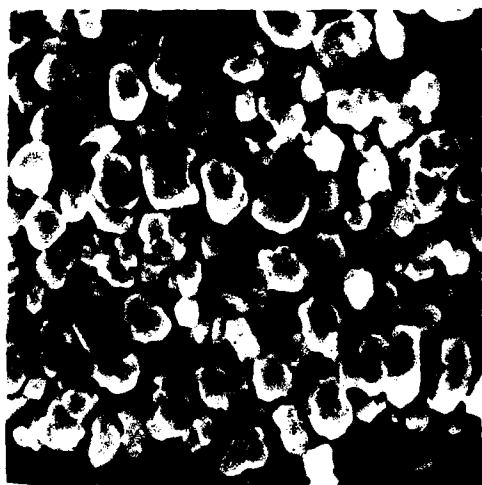
There is little doubt that small concentrations of the proper additives do alter the Ag deposit. The resistance of the plating is usually reduced and grain size and apparent density are changed. There is an optimum concentration level for the various additives which is a function of the substrate (enamel or ivory) and the chemical compositions (pH and type of silver salt) of the solutions involved.

Table VIII. Resistance ( $\Omega$ ) of Ag deposited on ivory or surface enamel as a function of the concentration of thiourea. [42.5%  $H_3PO_4$  etch, 100 g/l AgF or  $AgNO_3$  - sat.  $FeSO_4$  + x g/l thiourea ( $\sim 2$  pH) Ag - Fe seq.]

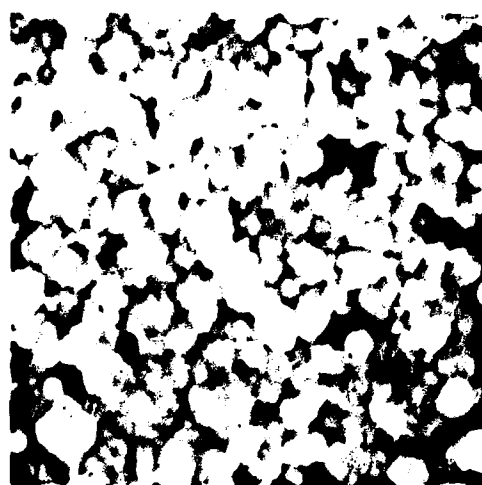
Thiourea concn. (g/l)	# Repeti- tions	Ivory		Surface Enamel	
		5.4 pH AgF	2.2 pH $AgNO_3$	3.3 pH AgF	6.6 pH $AgNO_3$
0	3X 5X 6X	$10^8$		5-50	0-5
0.01	3X 5X 6X	2-10	200	>500	>500
0.1	3X 5X 6X	10-30	150-1000	5-30	10-100
1.0	3X 5X 6X	2-5	$\infty$	5-100	50-500
10.0	3X 5X 6X	$\infty$	$\infty$	>500	>500

When properly chosen, the additives reduce the particle size and/or give a more continuous and dense deposit. Figures 1 and 2 show the effect of thiourea additions on the morphology of the deposits on ivory and enamel substrates respectively. The sequence Ag - Fe, rather than Ag - Fe - Ag was used in making these deposits. Without any addition, the micrograph indicates that the Ag deposit consists of large individual grains. With increasing additions of thiourea the grain size decreases and the deposit appears to become more dense and continuous and the conductivity increases. However, with further additions a limit is reached beyond which a white precipitate appears during deposition and the conductivity starts decreasing even though morphologically the deposit appears to be satisfactory. There is an optimum level of thiourea concentration and it appears to be 0.5 gpl with 3.3 pH AgF and 2 pH  $\text{FeSO}_4$  solutions on ivory substrates based on the morphological studies.

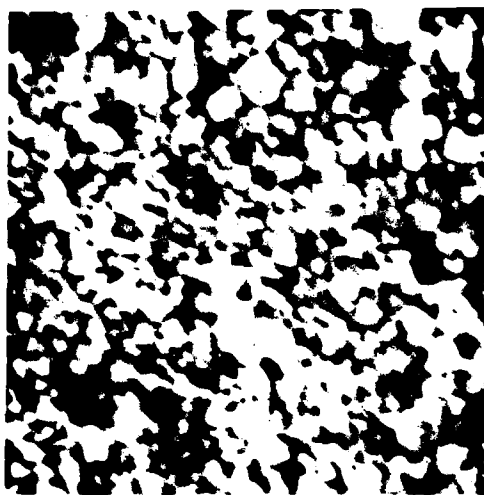
With 0.5 gpl thiourea in saturated  $\text{FeSO}_4$  solution, attempts were made to optimize the pH's of the silver and iron solutions on enamel. A small number of repetitions were used in these tests, since the effect of various parameters on deposit conductance decreases as the number of repetitions increases. The effect of thiourea on conductance is shown in Table IX at various  $\text{FeSO}_4$  pH's. The resistances of the deposits are lower with 0.5 gpl thiourea added to the  $\text{FeSO}_4$  solution than without any addition, on both the ivory and enamel substrates. Table X lists the effects of AgF pH and  $\text{FeSO}_4$  pH, with 0.5 gpl thiourea added to the reductant. The "rub" technique was used as an aid in screening. The optimum AgF pH appears to be about 5.3 for both ivory and enamel with 0.5 gpl thiourea added to  $\text{FeSO}_4$  solution. However, there might be a wider acceptable pH region for enamel from



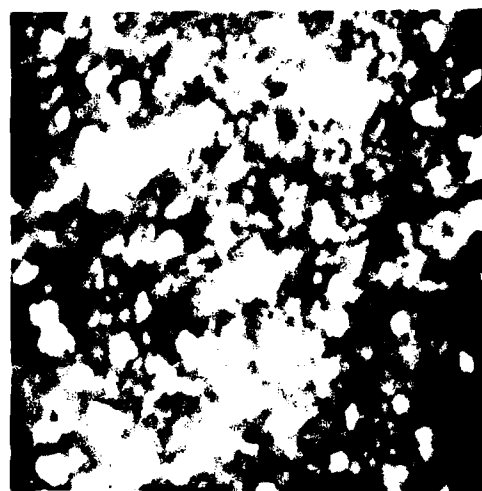
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b

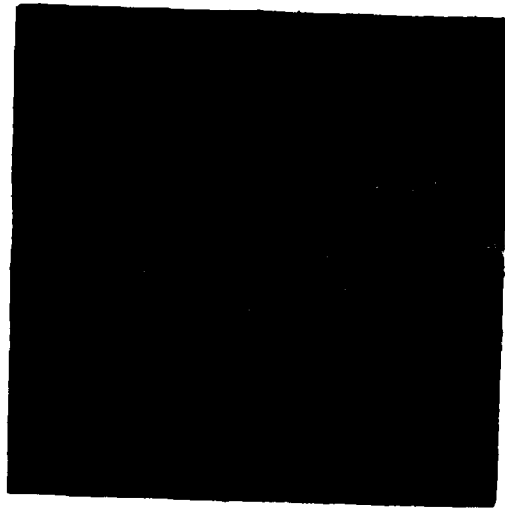


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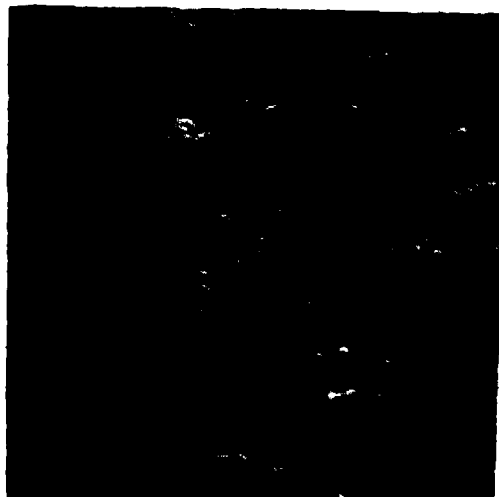
Figure 1. Surface morphologies after 5 repetitions of Ag deposits on ivory.  
[100 gpl AgF + HNO<sub>3</sub> (pH = 3.2) sat. FeSO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> (pH = 2), Ag - Fe seq.]  
Thiourea conc. a. 0 gpl b. 0.5 gpl c. 1 gpl d. 5 gpl  
magnification 3000X



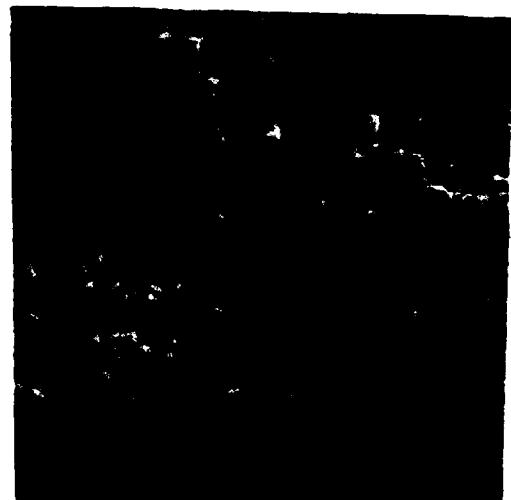
a



b



c



d

Figure 2. Surface morphologies after six repetitions of Ag deposits on enamel. [100 gpl AgF +  $\text{HNO}_3$  (pH = 3.3) sat.  $\text{FeSO}_4$  +  $\text{H}_2\text{SO}_4$  (pH = 2), Ag - Fe seq.] Thiourea conc. a. 0 gpl b. 0.01 gpl c. 0.1 gpl d. 1.0 gpl magnification 3000X

Table IX. Effect of  $\text{FeSO}_4$  pH, thiourea addition, and number of applications on the resistance of the Ag deposit on ivory and tooth enamel. Plating conditions: prereduction 1X [100 gpl  $\text{AgF} + \text{HNO}_3$  (4.5 pH), 30 sec - wash -  $\text{FeSO}_4$  solution with or without thiourea, 1 min - wash], standard application of [100 gpl  $\text{AgF} + \text{HNO}_3$  (4.5 pH) -  $\text{FeSO}_4$  solution with or without thiourea], 3X. ( $\text{Ag}^+ - \text{Fe}^{+2} - \text{Ag}^+$  seq.)

	Resistance, $\Omega$						Substrate	
	$\text{FeSO}_4 + \text{H}_2\text{SO}_4$ (2 pH)		$\text{FeSO}_4$ (3.6 pH)		$\text{FeSO}_4 + \text{NH}_4\text{OH}$ (5.4 pH)			
	w/o thiourea	with 0.5 gpl thiourea	w/o thiourea	with 0.5 gpl thiourea	w/o thiourea	with 0.5 gpl thiourea		
Prereduction		$2 \times 10^8$		$10^8$		$5.0 \times 10^7$	$2 \times 10^7$	Ivory
Standard 1X		$2.5 \times 10^7$	$10^7$	$2.0 \times 10^7$	$5 \times 10^7$	$6 \times 10^6$	$1.5 \times 10^7$	Ivory
Standard 2X			15	$10^6$	10	$6 \times 10^6$	$1.2 \times 10^7$	Ivory
Standard 3X		5	4	$1.5 \times 10^6$	4	$3 \times 10^7$	$\infty$	Ivory
Prereduction		$\infty$		$\infty$		$\infty$	$\infty$	Enamel
Standard 1X		$\infty$	500	$5.0 \times 10^7 - \infty$	15-100, 15-500	$\infty$	6,000	Enamel
Standard 2X			25	$1.5 \times 10^8$	2	$\infty$	15	Enamel
Standard 3X		$10^3 - 1.5 \times 10^8$	8	$700 - \infty$	0.8	$10^7 - \infty$	6	Enamel

Table X. Resistance of the Ag deposit as a function of pH of AgF and  $\text{FeSO}_4$  + 0.5 gpl thiourea solutions and number of applications on ivory and tooth enamel. Plating conditions: 100 gpl AgF +  $\text{HNO}_3$  or nothing -  $\text{FeSO}_4$  + 0.5 gpl thiourea +  $\text{H}_2\text{SO}_4$ , nothing, or  $\text{NH}_4\text{OH}$ , wash, rub technique. ( $\text{Ag}^+$  -  $\text{Fe}^{+2}$  seq.)

AgF pH →  FeSO <sub>4</sub> pH		Resistance, Ω												Substrate
		2.1			4.1			5.3			6.7			
		3x	5x	3x	5x	3x	5x	3x	5x	3x	5x	3x	5x	
2		∞	∞	40-∞	20-10 <sup>4</sup>	12	7	100	7	100	7	100	7	Ivory
3.7		∞	∞	20-∞	30-500	100	5	30-150	5	30-150	5	30-150	5-50	Ivory
5.5		∞	5x10 <sup>7</sup> Ω	150-∞	20-100	100	7	100-3000, 10 <sup>5</sup> -∞	7	100-3000, 10 <sup>5</sup> -∞	7	100-3000, 10 <sup>5</sup> -∞	15, 50-200	Ivory
2			∞		8-45		1						2	Enamel
3.7			∞		4		3						7	Enamel
5.5			∞		50		2						5	Enamel



~5.3 to ~6.7. From both Tables IX and X, it can be seen that  $\text{FeSO}_4$  pH is not significant and that there is a wide region of operation for both ivory and enamel. However, lower pH (~2) is preferred because  $\text{FeSO}_4$  becomes unstable as the pH increases.

The wear resistance of the Ag deposits on enamel obtained from the  $\text{FeSO}_4$  plus thiourea system and the original conditions used in plating monkeys are compared in Table XI. One set of the deposits was soaked in salt solution. The  $\text{N}_2\text{H}_4$  deposit is shown to be much better than the plain  $\text{FeSO}_4$  deposits. However, there was no significant difference between the two systems when the deposit was soaked in 0.86% saline solution. With the addition of 0.5 gpl thiourea to  $\text{FeSO}_4$ , the wear resistance of the deposits improved significantly and seems to be approaching  $\text{N}_2\text{H}_4$  deposit. The saline solution did not seem to have any deleterious effect as far as wear resistance is concerned, when thiourea was added to  $\text{FeSO}_4$ .

Since thiourea additions seem to improve the coverage of the substrate and the wear resistance of the deposit, it was decided to further optimize on its concentration. The results for tooth enamel are listed in Tables XII and XIII. According to Table XII, at 3X, thiourea addition of 0.1 gpl or more decreased the resistance of the deposit indicating better coverage. The wear resistance appears to be best at 0.3 gpl thiourea both at 3 and 10X, with  $\text{FeSO}_4$  pH of 2 and AgF pH of 5.4 on enamel.

## VII. APPLICATION TECHNIQUE

The technique of application of the two solutions probably influences the morphology of the deposit as shown in Figures 3 and 4. Figures 3a and 3b show the effect of lightly touching solutions as opposed to mixing them

Table XI. Wear numbers of Ag deposit on enamel for various systems. Conditions: 3/4" goat hair soft wheel brush, surface speed - ~80 cm/sec (800 rpm), force - 20 g, time - 60 sec. Plating conditions: ( $\text{Ag}^+$  -  $\text{Fe}^{+2}$  seq.), 10X.

System	Wear Numbers		Comments
	Unsoaked	Soaked in 0.86% saline solution for ~24 hr	
100 gp1 AgF (7 pH) - sat $\text{FeSO}_4$ + $\text{NH}_4\text{OH}$ (~6 pH)	2	1	similar conditions used for plating monkeys + amalgamated sample in saline turned yellow
100 gp1 AgF (7 pH) - sat $\text{FeSO}_4$ + $\text{NH}_4\text{OH}$ + 0.1 gp1 $\text{SnF}_2$ (~6 pH)	3	2	similar conditions used for plating monkeys + amalgamated sample in saline turned yellow
100 gp1 AgF + $\text{NH}_4\text{OH}$ (7 pH) - 10 ml/1 $\text{N}_2\text{H}_4$	6	2 <sup>a</sup>	similar conditions used for plating monkeys + brush plated (no amalgamation) sample in saline turned yellow
100 gp1 AgF + $\text{HNO}_3$ (4.5 pH) - sat. $\text{FeSO}_4$ + $\text{H}_2\text{SO}_4$ + 0.5 gp1 thiourea (2 pH)	3	7	
100 gp1 AgF + $\text{HNO}_3$ (5.4 pH) - sat. $\text{FeSO}_4$ + 0.5 gp1 thiourea (~3.6 pH) <sup>c</sup>	8 <sup>b</sup> 7 <sup>d</sup>	8 <sup>b</sup> 5 <sup>d</sup>	

- a. 7 hr. soak  
b. 0.5% NaF added to H PO etchant  
c. prereduced  
d. wear time was 30 sec.

Table XII. Effect of thiourea concentration on resistance and wear numbers of the Ag deposit on tooth enamel. Plating conditions: 100 gpl AgF + HNO<sub>3</sub> (5.5 pH) - sat FeSO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> + x gpl thiourea (2 pH), (Ag<sup>+</sup> - Fe<sup>+2</sup> - Ag<sup>+</sup> seq.), 3X. Wear test parameters: 3/4" goat hair soft wheel brush, surface speed ~80 cm/sec (800 rpm), force ~20 g, time 10 sec.

Thiourea Conc.	Resistance, $\Omega$			Wear #
	1X	2X	3X	
0.0	$\infty$	$1.1 \times 10^8$	250	2
0.01	$\infty$	$\infty$	260	2
0.1	$\infty$	1000	12	7
0.3	$\infty$	190	9	10
0.5	$\infty$	4000	7	2

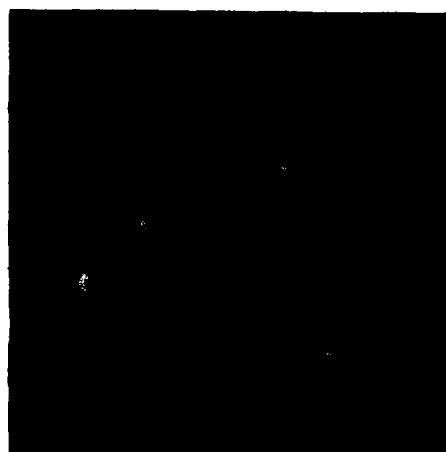
Table XIII. Effect of thiourea concentration and  $\text{FeSO}_4$  pH on resistance and wear numbers of Ag deposit on tooth enamel. Plating conditions: 100 gpl  $\text{AgF} + \text{HNO}_3$  (5.4 pH) - sat  $\text{FeSO}_4 + \text{H}_2\text{SO}_4$  or nothing, ( $\text{Ag}^+ - \text{Fe}^{+2} - \text{Ag}^+$  seq.), 10X. Wear test parameters: 3/4" goat hair soft wheel brush, surface speed ~80 cm/sec (800 rpm), force 20 g, time 60 sec.

Thiourea Conc.	$\text{FeSO}_4$ (3.6 pH)			$\text{FeSO}_4 + \text{H}_2\text{SO}_4$ (2 pH)		
	Resistance, $\Omega$		Wear #	Resistance, $\Omega$		Wear #
	5X	10X		5X	10X	
0.0	30	0.65	7			
0.05	28	0.36	8	25	0.65	7
0.1	2.8	0.22	9	4.3	0.47	7
0.3	6	0.22	6	1.2	0.10	9
				1.7 <sup>a</sup>	0.13 <sup>a</sup>	9 <sup>a</sup>
0.5	4.5	0.29	5	3.7	.25	8

a. enamel surface was polished on diamond wheel and 600 grit emery paper

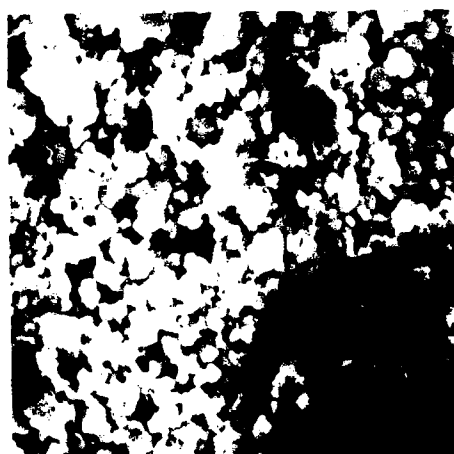


a.



b.

Figure 3. SEM micrographs showing the effect of solution application technique. [100 g/l AgF +  $\text{HNO}_3$  (5.4 pH) - sat.  $\text{FeSO}_4$  +  $\text{H}_2\text{SO}_4$  (2 pH), Ag - Fe seq., 10X.] Magnification 10,000X. a. Solutions lightly touched on the surface, and b. Solutions swabbed (or mixed) together on the surface.



a.



b.

Figure 4. SEM micrographs showing the effect of solution application technique. [100 g/l AgF (7 pH) - sat.  $\text{FeSO}_4$  +  $\text{NH}_4\text{OH}$  (5.5 pH), Ag - Fe seq., 10X.] Magnification 3,000X. a. Solutions swabbed (or mixed) on the surface, and b. Solutions swabbed (or mixed), washed, and the surface vigorously rubbed.

together with a swab (swabbing technique) on the surface. The former gives a deposit with particles which are relatively large and not bridged whereas the latter appears to have aggregates of smaller particles with more bridging. The effect of rubbing versus no rubbing is shown in Figure 4. The technique in the case of Figure 4a is similar to that of Figure 3b except that the pH conditions are different. The deposit shown in Figure 4b was vigorously rubbed after swabbing the two solutions together. This gives much smaller particles and a denser deposit. The swab plus rub technique seems to be beneficial since it reduces the localized concentration gradients. However, it probably introduces cold work in the deposit depending on the degree of rubbing.

A swab plus rub application technique helps in screening tests for variables.  $\text{FeSO}_4$  deposits obtained (without rubbing) over a wide range of AgF pH, viz. from 2 to 7.3, gave mixed results with respect to conductivity. However, with rubbing, intermediate pH AgF solutions gave deposits with low resistance while the low pH AgF solutions gave poor deposits with respect to conductivity; see Table XIV. The ivory and enamel substrates appear to behave similarly. At low AgF pH's the reduced silver came off with the swab after rubbing and did not seem to adhere to the surface. As the pH increased less and less silver was rubbed off the surface. It appears that AgF pH is critical to obtain a good deposit conductivity, while the  $\text{FeSO}_4$  pH is less sensitive. The optimum pH value for AgF appears to be about 6.8 when  $\text{FeSO}_4$  solutions of pH 2, 3.7, or 5.5 are used as reductant without any additive.

Table XIV. Resistance of Ag deposit on ivory or tooth enamel as a function of AgF pH,  $\text{FeSO}_4$  pH, and number of repetitions. "Rubbing" technique with  $\text{Ag}^+$  -  $\text{Fe}^{+2}$  sequence was used.

100 g/l AgF (pH) - Resistance ( $\Omega$ )									
$\text{FeSO}_4$ pH	$\sim 2.1$		$\sim 4.1$		$\sim 5.4$		$\sim 6.8$		$\sim 7.3$
	5X	10X	5X	10X	2X	5X	10X	2X	5X
IVORY									
$\sim 2.0$	$\infty$	$\infty$	$\infty$	$\infty$	$\infty$	$\infty$	$10^{-3}-1.5 \times 10^4$ & $\infty$	$\infty$	$\infty$
$\sim 3.7$	$\infty$	$\infty$	$\infty$	$\infty$	$\infty$	$\infty$	$10^6-\infty$	$5 \times 10^2-2 \times 10^3$	10-200
$\sim 5.5$	$\infty$	$\infty$	$\infty$	$\infty$	$2 \times 10^6-\infty$	$5 \times 10^5-\infty$	$1.5 \times 10^7$	$\infty$	10-200
ENAMEL									
$\sim 2.0$	$\infty$	$\infty$	$\infty$	$\infty$	$\infty$	$\infty$	20	$\infty$	$\infty$
$\sim 3.7$	$\infty$	$\infty$	$\infty$	$\infty$	$1 \times 10^3-1.5 \times 10^4$	$20-2 \times 10^5$	$\infty$	$\infty$	$\infty$
$\sim 5.5$	$\infty$	$\infty$	$\infty$	$\infty$	$4 \times 10^5$	4-200	$\infty$	$\infty$	$\infty$

### VIII. RATE STUDIES

The properties that influence the wear characteristics of Ag deposits are hardness, morphology, and apparent density. The amount of Ag in the deposit or the film thickness is also important in that it makes the film last longer. For this, the rate of Ag deposition on the substrate needs to be studied.

Two different techniques were used for rate studies. In the first, the entire surface of the sample - ivory or tooth enamel - is plated. The deposit is then masked using a punched tape and only the exposed surface is dissolved. In the second technique only the area to be plated is exposed, the remainder of the surface being masked by tape. The tapes used were regular masking tape and an electroplater's tape. Both of them worked satisfactorily on a flat surface like ivory; however, for enamel, the electroplater's tape is preferred since it minimized solution penetration at the circle edge.

The dissolving medium was 50 vol % concentrated  $\text{HNO}_3$  (35 wt %  $\text{HNO}_3$ ). This concentration is desired since the problems associated with the dissolution of the deposit appear to be minimized. With a lower concentration, like 25 vol % concentrated  $\text{HNO}_3$  (7.5 wt %  $\text{HNO}_3$ ), the length of time the acid remains on the surface is longer, which increases the formation of a yellow film of  $\text{Ag}_3\text{PO}_4$ . With concentrated  $\text{HNO}_3$ , the likelihood of more apatite dissolution increases, which might increase the possibility of more  $\text{Ag}_3\text{PO}_4$  formation. The solutions containing the dissolved silver were prepared for atomic absorption analysis by diluting with water and adjusting the pH to  $\sim 1.5$  with 1 vol % concentrated  $\text{HNO}_3$ .

Some rate study results on ivory obtained using glucose as the reducing agent are given in Table XV. Only an area of 1/4 inch circle was plated.



Table XV. The rate of Ag deposition on ivory as a function of glucose pH  
(0.317 cm<sup>2</sup> area plated, Ag - glucose seq., 10X)

pH of 100 gpl AgF	pH of 400 gpl glucose with NaOH	
	11.6 mg/cm <sup>2</sup>	12.2 mg/cm <sup>2</sup>
6.8	1.76	2.31
7.35	1.55	2.34
7.6	1.52	1.72
7.85	1.73	1.99
9.0	1.37	1.78

The rate of Ag deposition seems to increase with increasing pH of the glucose solution whereas it decreases with increasing pH of the silver solution.

The rates of Ag deposition on tooth enamel using  $\text{FeSO}_4$  + thiourea reductant with and without prereduction are given in Table XVI for multiple samples. Also listed in the table are resistance and wear numbers. The rates appear to be low compared to the values reported earlier for  $\text{FeSO}_4$  system, but this is probably due to the difference in technique used. In this case, the entire enamel surface of a half-ground tooth was plated and an area equivalent to 1/8 inch diameter only was dissolved. The rate of Ag deposition increased with prereduction which might be partly due to an extra application of  $\text{Ag}^+$  solution during prereduction. The wear characteristic did not improve with prereduction. The reproducibility, as reflected in the standard deviation, appears to be acceptable, except for wear. But this might be expected considering the inherent differences from one tooth to another and the qualitative evaluation involved. However, efforts will be made to improve upon it. Additional work is also needed to determine the quantity of silver deposited during each repetition and the influence of area plated on rate.

The influence of thiourea on the rate of Ag deposition on ivory is shown in Table XVII, as a function of AgF pH. With the addition of the thiourea the rate increased significantly being in excess of 100% with AgF pH of 5.1 or less. At a pH of 6.85 the increase was substantially less (10%). However, the rate decreased with decreasing pH without thiourea addition. Resistance values are also given in the table and these show a decrease with thiourea addition.

Table XVI. Resistance, wear number, and rate of Ag deposition<sup>a</sup> and their reproducibility<sup>b</sup> with and without prereduction on tooth enamel. Plating conditions: 125 gpl AgF + HNO<sub>3</sub> (6 pH) - sat. FeSO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> + 0.18 gpl thiourea (2 pH), (Ag<sup>+</sup> - Fe<sup>+2</sup> - Ag<sup>+</sup> seq.), 10X. Wear test conditions: 0.7 inch diameter goat hair soft wheel brush, surface speed 20 cm/sec (208 rpm), force 20 g, time 2 min.

Technique	Resistance, $\Omega$	Wear #	Rate, mg/cm <sup>2</sup>
Standard with thiourea	0.18, 0.59, 0.49, 0.20, 0.34 (0.36 $\pm$ 0.18)	8, 8, 4, 5, 6 (6.2 $\pm$ 1.8)	1.04, 1.16, 1.27, 1.10 (1.14 $\pm$ 0.10)
Prereduction + Standard with thiourea	0.16, 0.12 (0.14 $\pm$ 0.03)	7, 5 (6 $\pm$ 1.4)	2.96, 1.25 (2.10 $\pm$ 1.21)

- Rate studies were done by plating the enamel first and then selectively dissolving by taping (hole diameter in the tape - 1/8").
- Mean and standard deviation are given in parentheses.

Table XVII. Effect of Thiourea and AgF pH on the Rate of Ag Deposition on Ivory. Plating Conditions: 100 gpl AgF (pH varying) - sat.  $\text{FeSO}_4 + \text{H}_2\text{SO}_4 + 0$  or  $0.25$  gpl thiourea (2 pH), 10X,  $1/4$ " dia. circle plated.

AgF pH	Thiourea (gpl)	Resistance ( $\Omega$ )	Rate (mg of Ag/cm <sup>2</sup> )	% increase with thiourea
6.85	0.25	0.17	2.63	10.5
6.85	0.0	0.54	2.38	--
5.1	0.25	0.37	3.59	103
5.1	0.0	10.36	1.77	--
1.8	0.25	0.48	3.75	119
1.8	0.0	~24	1.71	--

## IX. SHEAR TESTS

### A. Shear Strength of Deposits

In order to evaluate the deposits, amalgamation and shear tests were conducted on both ivory and enamel substrates and the results are given in Table XVIII. Some of the deposits were brush plated using silver or tin solutions. The samples were not polished on sandpaper and the results are scattered. This is probably due to a number of factors, the primary ones being the amalgamation technique and uncontrolled thickness of the samples. Efforts are underway to improve this by the use of an air-driven amalgam condenser. Various alloys were used, viz. Optaloy, Caulk Spherical, and Oraloy. Also these alloys might behave differently depending on the amount of mercury and the types and amounts of phases formed.

The average shear test results are given in Table XIX, as a function of the treatment and the type of amalgam. Also indicated in parentheses are the spread of the values. The average values given do not include the zero shear stresses that were sometimes obtained, as it was felt that this was caused by poor amalgam practice. The results indicate that the prereduction increases the adherence of the deposit slightly over that of the standard procedure. (In these prereduced deposits, there is only one prereduction step, and the remaining repetitions consist of both AgF and FeSO<sub>4</sub> applications.) With thiourea as an additive, the adherence of the deposit increases considerably, which indicates that a continuous and dense deposit is highly desirable. Prereduction with Fe containing thiourea further increases the shear stress slightly. It appears from these results that the deposits obtained using an additive and prereduction are approaching the reference deposits of the N<sub>2</sub>H<sub>4</sub> system (see Table XIX).

Table XVIII

Shear Tests

AgF-Glucose System (Ag-Glucose Seq.)

pH of 100 gpl AgF	pH of 400 gpl Glucose	Shear Stress (psi)		# of samples
		Avg.	Range	
7.3	11.6	127	0-550	19
7.3	11.6 <sup>a</sup>	194	0-720	6
7.3	12.2	194	49-477	3
7.3	12.2 <sup>b</sup>	456	--	1
5.4	11.6	49	--	1
6.2	11.6	262	--	1
6.8	11.6	175	0-519	4
9.1	11.6	275	0-674	8
10	11.6	123	--	1

a. Brush plating following standard plating sequence

b. 30 repetitions

Table XVIII continued

AgF-Hydrazine System (Ag-N<sub>2</sub>H<sub>4</sub> Seq.)

pH of 100 gpl AgF	Shear Stress (psi)		# of samples
	Avg.	Range	
7.3	161	0-333	10
7.3	272 <sup>a</sup>	--	1
7.3	209 <sup>b</sup>	98-318	3
8.1	270	102-408	4
8.1	227 <sup>b</sup>	71-408	5

a. 30 repetitions

b. electroless followed by brush plating

Table XVIII continued

AgNO<sub>3</sub>-FeSO<sub>4</sub> System (Ag-Fe Seq.)

pH of sat. FeSO <sub>4</sub>	pH Range of 100 gpl AgNO <sub>3</sub>	Shear Stress (psi)		# of samples
		Avg.	Range	
2	2.30-6.6	500	175-1158	6
5.8	2.80	0	--	1

Table XVIII continued

AgF-FeSO<sub>4</sub> System (Ag-Fe Seq.)

pH of sat. FeSO <sub>4</sub>	pH Range of 100 gpl AgF	Shear Stress (psi)		# of samples
		Avg.	Range	
2.1	1.7	396	--	1
5.5	6.2-7.3	191	0-500	5

Table XIX

Shear Test Results on ivory substrate<sup>a</sup> (42.5% H<sub>3</sub>PO<sub>4</sub> etch, WB, Ag - Fe sequence, 10X. WB.)  
Amalgam Condensed by Hand

I. 100 gp1 AgF + HNO<sub>3</sub> (-3.8 pH) -sat. FeSO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> (2 pH) System

Method of Application	Shear Stress (psi)			
	Oraloy	"Op"	Optaloy "C"	"B" "Op"
Standard <sup>b</sup>	672±406 (4, 0-1025)	872	895	376 337
Standard Reverse <sup>c</sup>		657	265	294
Prereduction <sup>d</sup> + Standard <sup>b</sup>	732±427 (3, 0-1167)			
Standard <sup>b</sup> (using .5 gp1 thiourea in reducing solution)	1284±889 (6, 0-2887)			
Prereduction <sup>d</sup> + Standard <sup>b</sup> (using .5 gp1 thiourea in reducing solution in both steps)	1396±742 (3, 0-1920)			

II. 100 gp1 AgF + NH<sub>4</sub>OH (7.3 pH) -10ml/1 N<sub>2</sub>H<sub>4</sub> System

Standard <sup>a</sup>	1397±249 (7, 0-1700)	728±239 (3, 0-1000)	602±492 (4, 0-1333)	278
Standard Reverse <sup>b</sup>			964	

a. Shear stress values of 0 psi are not considered in the calculation of average or the standard deviation.  
Number of samples with non-zero stress and the spread of values are given in parenthesis.

b. Standard procedure of plating: Ag<sup>+</sup> solution - reducing solution.

c. Standard reverse: reducing solution - Ag<sup>+</sup> solution.

d. Prereduction: Ag<sup>+</sup> solution - water wash - reducing solution.



Also the two different amalgams used give different shear stress values, the Oraloy being superior to Optaloy. This may be due to the lower Hg content of Oraloy.

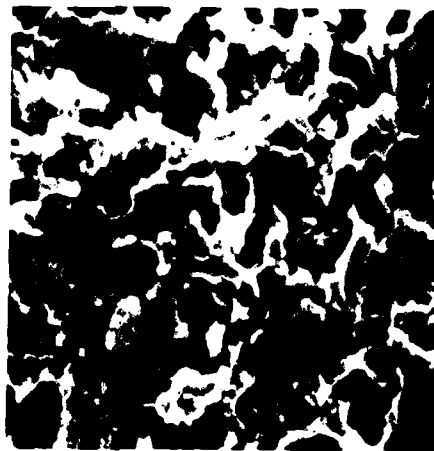
Efforts are continuing to investigate the apparent zero stress results. Figure 5 shows the SEM micrographs of amalgamated spots obtained after the shearing. The spots had a layer of amalgam in some areas and these areas indicate that the amalgam which gave a shear stress of 1167 psi is more dense compared to the one which had a shear stress of 0 psi. The latter is porous.

#### B. Shear Strength of the Amalgam

It has been noted that there is a large variation in the shear strength values obtained on a single test piece. In order to see if the amalgamation procedure was largely responsible for this variation, tests were performed to find the shear strength of the amalgam/amalgam interphase. A disc (5/8 inch diameter x 1/8 inch thick) of 20th Century Fine Cut amalgam was prepared. After setting for 24 hours at room temperature, a small cylinder of the same amalgam was condensed on disc surface after it was wet polished and dried. The cylinder was sheared from the disc after 24 hours and the strength calculated. From the average shear stress, which was found to be  $2692 \pm 918$  psi, it can be seen that there is a large variation (34%) in the shear stress of the amalgam/amalgam interphase from one trial to another. This indicates that the amalgamation procedure is susceptible to considerable variation and in turn is responsible to a great extent for the wide scatter of the shear stress values at the amalgam/plated Ag interphase.



a



b

Figure 5. SEM micrographs of the sheared amalgam (Oralloy) spots on ivory deposited with silver. Magnification 3000X. Shear stress: a. 1167 psi, and b. 0 psi.

## X. BRUSH PLATING

Brush plating is a technique whereby localized electrodeposition is possible without total immersion in a plating bath. Electrical energy for the process is supplied from a small DC rectifier or battery. The piece to be plated, in this case the tooth which has been previously coated by the electroless process, is made the cathode (or negative). The anode consists of a pencil shaped insulated body with a conductive metal rod through the center. A silver wire is attached to the rod and serves as the plating stylus. The assembly tip is then wrapped in an absorbent material (such as cotton or cheesecloth) which can contain the electrolyte. The anode stylus is touched to the area to be plated, being careful to insure that only the absorbent material and not silver wire comes in contact with the tooth. The negative lead can be touched to any part on the conductive tooth, but plating occurs only under the anode where there is electrolyte present.

Plating conditions can be varied to obtain the properties desired. Current density, time, electrolyte composition, and additives are a few of the variables that can be readily changed.

Thus far, silver has been the principal metal applied in the brush plating tests. The electrolyte has been mostly silver fluoride with supplemental additions of thiourea, thiosulfate, and thiocyanates. SEM and wear tests were then made on films, using these solutions at different operating conditions. Plating voltages are generally low (in the 0.2 to 0.4 V range) and should not present any problems in commercial usage.

The results and conditions of brush plating tests on electroless Ag substrate are listed in Tables XX and XXI. The substrate was obtained by the use of glucose and  $\text{FeSO}_4$  reducing agents. The electroplated deposits were evaluated for the wear resistance and shear stress. The tables show some of the parameters involved. Since these tests were the beginning trials and only one sample was used for each run some of the conclusions could be premature. More experiments are needed to allow more definitive judgements. However, following are the general observations noted.

The wear resistance of the deposit decreases as the current density decreases. However, this may be due to the decreasing amount of Ag deposited as the current density decreases, and not a direct indication of current density per se. The addition of KI, thiourea, or  $(\text{NH}_4)_2\text{S}_2\text{O}_3$  did not seem to have any particularly beneficial effect. The shear stress values were scattered over a wide range with quite a few zero values which was probably due to the combination of the nature of the deposit and amalgamation technique. In general, with the use of rub technique during the electroless procedure, it was relatively more difficult to brush plate than when the non-rub technique was used.

The morphologies of the brush plated deposits, shown in Figures 6-8, are quite varied depending on the plating conditions. A hydrazine type smooth deposit is obtained when only thiourea and the ammonium thiosulfate are added to AgF (Figure 6). However, when a large amount of KSCN is added to AgF the deposit becomes very densely packed with small grains or crystallites (Figure 7). The influence of certain process parameters on crystallization is shown in Figure 8. There is a decrease in crystallite size with decreasing current density for plating solutions containing  $\text{SnSO}_4$ .

Table XX. Results of Brush Plating Tests (Plating Time ~3 Min.) on Ivory. (Electroless Substrate Conditions: 100 gpl AgF or AgNO<sub>3</sub> (6.2-10 pH) - 400 gpl glucose + NaOH (11.6-12.1 pH), 10X with final rinse only, Ag-glucose seq. Wear Conditions: 0.7" dia. goat hair soft wheel brush, surface speed 20 cm/sec (208 rpm), force 28 g, varying time. Caulk fine cut alloy used for amalgamation. Approximate area under the plating brush 0.55 cm<sup>2</sup>.)

Electrolyte			Rel. Wear No.					
AgF (gpl)	KSCN or NH <sub>4</sub> SCN (gpl)	Additives (gpl)	Current (mA)	Voltage (volts)	Time (sec)			Shear Stress (psi)
					60	90	120	
15	300 <sup>a</sup>	15 <sup>b</sup> 0.4 <sup>c</sup>	5	0.4	5	1		55, 243
15	300 <sup>a</sup>	15 <sup>b</sup> 0.4 <sup>c</sup>	10 <sup>d</sup>	0.3-0.4	10		10	0
17	308 <sup>a</sup>	0.2 <sup>c</sup>	5-4	0.5	8		7 <sup>e</sup>	329, 0
17	300 <sup>f</sup>		15-20	0.6	10	8	7	489 <sup>g</sup> , 884
17	300 <sup>f</sup>		11-7	0.4	5			0 <sup>g</sup> , 0, 507, 471
17	300 <sup>f</sup>		2-5	0.25				861

Table XX. Continued.

Electrolyte			Rel. Wear No.					
AgF (gpl)	KSCN or NH <sub>4</sub> SCN (gpl)	Additives (gpl)	Current (mA)	Voltage (volts)	Time (sec)			Shear Stress (psi)
					60	90	120	
17	300 <sup>f</sup>	0.2 <sup>c</sup>	10-3	0.4	4			0 <sup>g</sup> , 1100
17	300 <sup>f</sup>	0.2 <sup>c</sup>	5-2	0.25	0			1150, 910
17	300 <sup>f</sup>	0.4 <sup>c</sup>	7-11	0.4	0			690, 583
17	300 <sup>f</sup>	0.4 <sup>c</sup>	3	0.25				374, 328
17	250 <sup>f</sup>		4-5	0.2	8	8		800
17	250 <sup>f</sup>	0.2 <sup>h</sup>	9-10	0.25	8	7		0
17	250 <sup>f</sup>	0.2 <sup>i</sup>	4-5	0.2	8	0		552
17	250 <sup>f</sup>	0.2 <sup>i</sup>	7-10	0.35	8	0		
17	191 <sup>f</sup>	0.4 <sup>h</sup>	3-5	0.2	6			0
17	191 <sup>f</sup>	0.4 <sup>i</sup>	3-5	0.2	5			

Table XX. Continued.

Electrolyte			Rel. Wear No.			
AgF (gpl)	KSCN or NH <sub>4</sub> SCN (gpl)	Additives (gpl)	Current (mA)	Voltage (volts)	Time (sec)	
					60	90 120
17	291 <sup>a</sup>	0.2 <sup>c</sup> 1.0 <sup>i</sup>	5-7	1.0	0	1544 <sup>g</sup>
17	291 <sup>a</sup>	0.2 <sup>c</sup> 1.0 <sup>i</sup>	5-7	1.0	3	250 <sup>g</sup>
20	291 <sup>a</sup>	0.2 <sup>c</sup> 1.0 <sup>i</sup>	8-9	1.0	9 7	307 <sup>g</sup>
20	300 <sup>a</sup>	0.4 <sup>c</sup> 36 <sup>j</sup>	7-4	0.7	10	8 <sup>e</sup> 0 <sup>g</sup>
20	300 <sup>a</sup>	0.16 <sup>c</sup> 36 <sup>j</sup>	9-7	0.5	8	5 <sup>e</sup> 567 <sup>g</sup>
20	300 <sup>a</sup>	0.16 <sup>c</sup> 36 <sup>j</sup>	14-8	0.8	10 10 8	973
20	300 <sup>a</sup>	0.4 <sup>c</sup> 25 <sup>b</sup>	5.5-4.5	0.5	8 1	693

Table XX. Continued.

Electrolyte		Current (mA)	Voltage (volts)	Rel. Wear No.			Shear Stress (psi)
AgF (gp1)	KSCN or NH <sub>4</sub> SCN (gp1)			Time (sec)			
				60	90	120	
20	300 <sup>a</sup>	3-4	0.35	7	0	0 <sup>g</sup> , 0	
20	300 <sup>a</sup>	10-4	0.7	9	8	5	
						467, 1489	
25		5-6	1.5		6 <sup>e</sup>	0	

- a. KSCN was added.
- b. SnF<sub>2</sub> was added.
- c. KI was added.
- d. The sample was electroplated for 10 min.
- e. 14 g force used for wear.
- f. NH<sub>4</sub>SCN was added.
- g. Oralloy alloy was used for amalgamation.
- h. Thiourea was added.
- i. (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was added.
- j. SnSO<sub>4</sub> was added.



Table XXI. Results of Brush Plating Tests (Plating Time ~3 Min.) on Ivory. (Electroless Substrate Conditions: 100 gpl AgF + HNO<sub>3</sub> (5.5 pH) - sat. FeSO<sub>4</sub> + 0.5 gpl thiourea + NH<sub>4</sub>OH (5.5 pH), 10X with final rinse only, Ag-Fe-Ag seq. Wear Conditions: 0.7" dia. goat hair soft wheel brush, surface speed 20 cm/sec (208 rpm), force 28 g, varying time. Caulk fine cut alloy was used for amalgamation. Approximate area under the plating brush 0.55 cm<sup>2</sup>.)

Electrolyte			Rel. Wear No.					
AgF (gpl)	KSCN (gpl)	Additives (gpl)	Current (mA)	Voltage (volts)	Time (sec)			Shear Stress (psi)
					60	90	120	
17	308		2-11	1-4	4			0 <sup>a</sup>
17	308		5-3	1.0	8	5		731, 0, 529
17	308		5-6	1.5			6 <sup>b</sup>	
17	308	0.2 <sup>c</sup>	8-2	3-1	9	4		929, 857 <sup>a</sup>
20	300	0.04 <sup>c</sup> 36 <sup>d</sup>	5-3	0.6	10	8		0, 1410
20	300	0.06 <sup>c</sup> 36 <sup>d</sup>	2-3	0.5	7	8	7	0
20	300	0.06 <sup>c</sup> 36 <sup>d</sup>	5-6	1.0	9	4		
20	300	0.06 <sup>c</sup> 36 <sup>d</sup>	11	1.5		2	8	0, 0

Table XXI. Continued.

Electrolyte			Rel. Wear No.					Shear Stress (psi)
AgF (gpl)	KSCN (gpl)	Additives (gpl)	Current (mA)	Voltage (volts)	Time (sec)			
					60	90	120	
20	300	0.06 <sup>c</sup> 36 <sup>d</sup>	11-4	1.0	8			0, 233 <sup>a</sup>
20	300	0.04 <sup>c</sup> 36 <sup>d</sup>	4-5.5	0.5	4			0 <sup>a</sup>
25		0.03 <sup>e</sup> 0.03 <sup>f</sup>	5-2	2.8	4 <sup>a</sup>			
25		0.03 <sup>e</sup> 0.03 <sup>f</sup>	5-2	2.8	9	7		0, 0
25 <sup>g</sup>		0.2 <sup>e</sup> 0.03 <sup>f</sup>	5-2	3-4	4			0 <sup>a</sup>
25 <sup>g</sup>		0.2 <sup>e</sup> 0.03 <sup>f</sup>	5-2	2.8	8	5		0, 0
SILV-R-COTE (commercial)								
			9	0.6	9	9	8	0, 382 <sup>h</sup> , 1478, 1087

Table XXI. Continued.

- a. Rub technique was used for electroless deposit.
- b. 14 g force was used for wear.
- c. KI was added.
- d.  $\text{SnSO}_4$  was added.
- e. Thiourea was added.
- f.  $(\text{NH}_4)_2\text{S}_2\text{O}_3$  was added.
- g.  $\text{AgNO}_3$  was used.
- h. Oralloy was used for amalgamation.

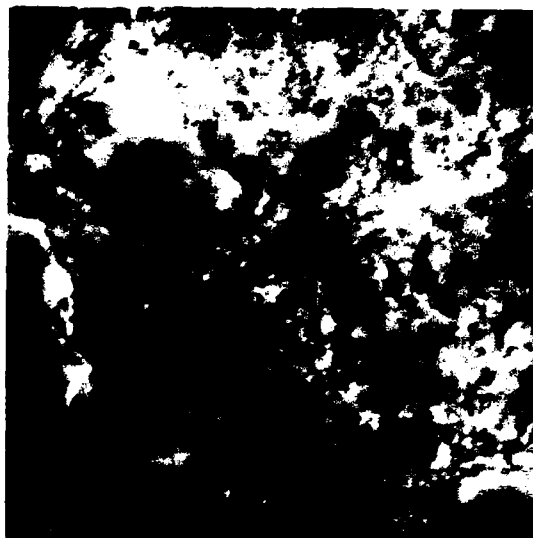


Figure 6. Brush plated deposit from 25 gpl AgF + 0.03 gpl thiourea + 0.03 gpl  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  solution at 3.7-9.2 mA/cm<sup>2</sup> and 2.8 V for 3 min. Electroless system: 42.5%  $\text{H}_3\text{PO}_4$  etch, 100 gpl AgF +  $\text{HNO}_3$  (5.5 pH) - sat.  $\text{FeSO}_4$  +  $\text{NH}_4\text{OH}$  + 0.5 gpl thiourea (5.5 pH), 10X.

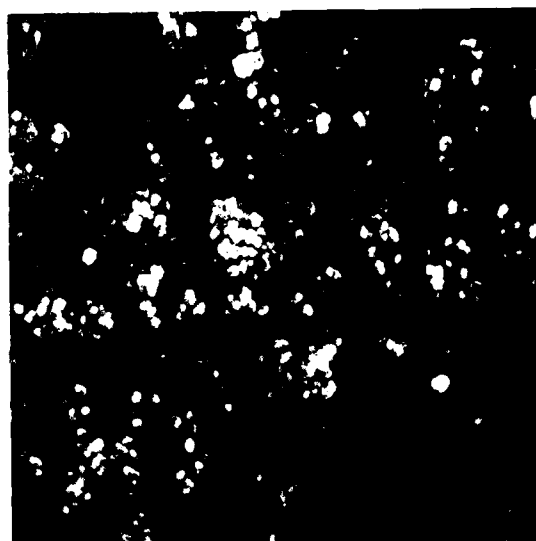
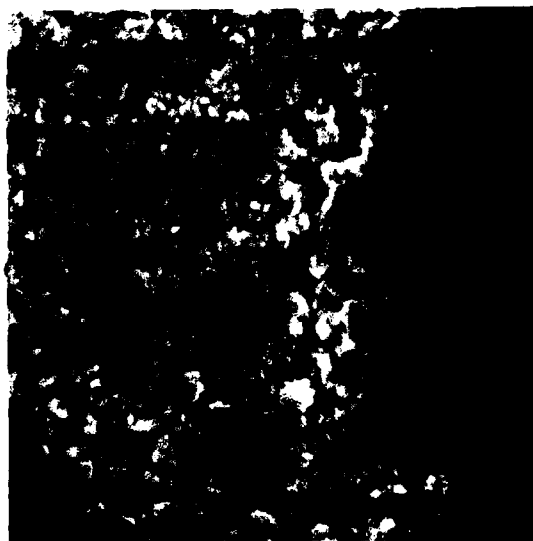
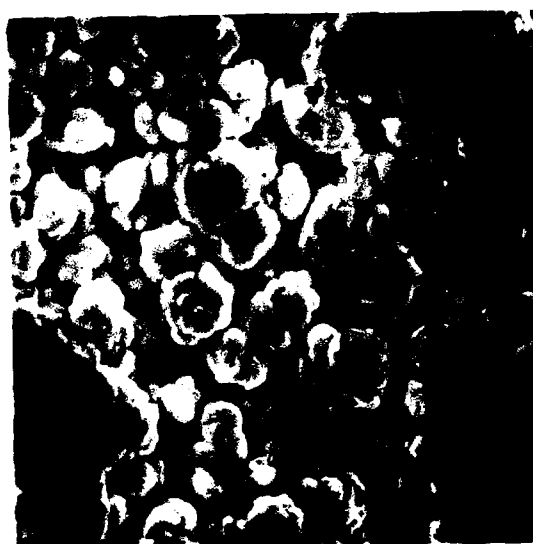


Figure 7. Brush plated deposit from 17 gpl AgF + 308 gpl KSCN + 0.2 gpl KI solution at  $\sim 8.3$  mA/cm<sup>2</sup> and 0.5 V for 3 min. Electroless system: 2.4 M  $\text{NH}_4\text{F}$  etch, 100 gpl  $\text{AgNO}_3$  +  $\text{NH}_4\text{OH}$  (9.2 pH) - 400 gpl glucose + 1 M NaOH (12.1 pH), 10X.



a



b

Figure 8. Brush plated deposits from 20 gpl AgF + 36 gpl SnSO<sub>4</sub> + 300 gpl KSCN + 0.06 gpl KI solution at 1.5 V for 2 min. (a. 4.6 mA/cm<sup>2</sup> and b. 20.4 mA/cm<sup>2</sup>). Electroless system: 42.5% H<sub>3</sub>PO<sub>4</sub> etch, 100 gpl AgF + HNO<sub>3</sub> (5.5 pH) - sat. FeSO<sub>4</sub> + NH<sub>4</sub>OH + 0.5 gpl thiourea (5.5 pH), 10X.

and KI. It is possible that Sn may co-deposit at the higher current densities, thus the observed effect may be due only indirectly to current density. The possibility of the co-deposition of other cations and their influence on crystallization and film properties requires additional evaluation. The type of electroless Ag substrate might also have an effect on the nature of the brush plated deposit, although this has not been studied.

## XI. STATISTICAL SCREENING

There are numerous variables involved in the electroless deposition of metals, such as solution concentrations and pH of  $\text{Ag}^+$  and  $\text{FeSO}_4$  solutions, concentration and type of additive, temperature, residence time, etchant and its concentration, etching time, prior treatment of the teeth, number of repetitions, sequence of application, and so on. It is difficult and time consuming to evaluate and optimize the system using the classical "single variable at a time" approach. Also it is possible that some of the variables may interact synergistically which will further complicate the system. Statistical experimental design should help in identifying the critical variables and reduce the time for optimization, and might also indicate interacting parameters.

An eight run Plackett-Burman type design was used to screen six variables.<sup>1-3</sup> The upper and lower limits and the center points of the variables are listed in Table XXII. The responses evaluated were conductance, rate of Ag deposition, wear resistance and shear strength of the deposit. The results of such a statistical design for the  $\text{AgF} - \text{FeSO}_4$  system on ivory substrate are given in Table XXIII. For more details and calculations, refer to the fourth quarterly report for 1978-79. The confidence level computed indicates if a particular variable is significant

Table XXII. Variables and the Limits

Variables	Lower Limit, (-)	Upper Limit, (+)	Center Points
$x_1$ , AgF concentration (g/l)	50	100	75
$x_2$ , pH of AgF	1.5, 1.85 <sup>a</sup>	5.3, 5.1 <sup>a</sup>	4.2
$x_3$ , pH of saturated FeSO <sub>4</sub>	2.0	3.5, 3.35 <sup>a</sup>	2.7
$x_4$ , thiourea concentration (g/l)	0.0	0.5	0.25
$x_5$ , residence time (sec)	30	90	60
$x_6$ , application technique	no rub	rub	medium rub
$x_7$ , dummy			

a. The pH limits changed after aging the solutions (even though they were the same after initial adjusting).

Table XXIII. Summary of Statistical Screening of Variables for Electroless Ag Deposition on Ivory (AgF-FeSO<sub>4</sub> system, refer to the fourth quarterly report for 1978-79).

Responses →  Variables	Conductance		Rate		Wear Resistance		Shear Stress	
	Main Effect Estimate $\Omega^{-1}$	Confidence Level (%)	Main Effect Estimate (mg/cm <sup>2</sup> )	Confidence Level (%)	Main Effect Estimate	Confidence Level (%)	Main Effect Estimate (psi)	Confidence Level (%)
X <sub>1</sub> , AgF Conc. (gpl)	1.58	48	0.83	>99	0	<20	381	90
X <sub>2</sub> , AgF pH	1.31	42	0.54	>99	1.0	36	447	92
X <sub>3</sub> , Sat. FeSO <sub>4</sub> pH	-3.81	74	-0.33	>99	0	<20	-541	94
X <sub>4</sub> , Thiourea Conc. (gpl)	4.66	78	1.00	>99	4.5	68	303	88
X <sub>5</sub> , Residence Time (sec.)	1.12	36	-0.29	>99	0	<20	183	80
X <sub>6</sub> , Application Technique	6.93	84	0.63	>99	-2.5	50	105	70
X <sub>7</sub> , Dummy	-1.67	50	-0.0025	50	2.5	50	55	50



or not for the response evaluated. A confidence level of 70% or more (70% is chosen arbitrarily) means that the variable is significant, and if it is less than 70% the variable is not significant. This will help in eliminating nonsignificant variables for further optimization.

According to the results of this design, the significant variables with respect to conductance are  $\text{FeSO}_4$ , pH, thiourea addition, and the application technique; the other variables do not have any significant effect. Also the positive value of the main effect estimate for thiourea concentration indicates that the conductance of the deposit is increased by increasing the thiourea concentration from 0 to 0.5 gpl. Similarly rubbing technique increases the conductance as opposed to no rubbing. The negative effect estimate for  $\text{FeSO}_4$ , pH indicates that the conductance can be increased by using low pH  $\text{FeSO}_4$ . For wear resistance the only variable close to being significant is thiourea concentration and it indicates that addition of 0.5 gpl thiourea improves wear. With respect to rate of Ag deposition and shear strength all the six variables have significant effect. Again the positive effect estimates indicate preference for the upper limits of the variables whereas the negative effect estimates show a preference for the lower limits. Some of these results agreed with the previous observations while others did not. One possible explanation for the disagreement might be the large variations in response measurements. Therefore an increased sample size for each run might give better agreement.

## XII. CONCLUSIONS

Reasonable strides have been made during the past year toward producing a silver deposit employing a non-toxic reducing agent with properties

approaching those obtained when hydrazine is used. One of the major revelations of the most recent research is the strong interrelationship that exists among the operating parameters used in the electroless plating process. Relatively small changes in the chemistry of the system (including concentration, pH, etc.) can produce very measurable effects on the silver film. It had been speculated in the past that addition agents might prove beneficial in the electroless plating and that was proven to be true. The use of thiourea with  $\text{FeSO}_4$  gave deposits that approached hydrazine type films, and this opened up a potentially exciting area to investigate. The system has been shown to be chemically flexible with respect to the ability to alter and improve the observed properties. Often, the chemistry that gives the best results for one property may well not yield the maximum for another. It is thus becoming obvious that the final desired use will dictate the specific process conditions to be used. For example, samples which give the better morphology or wear resistance may not necessarily have the maximum shear strength for amalgam.

Fortunately, the process has now matured to the point that optimization screening tests are possible. Distinct trends in the effects of various process variables on silver properties were established based on statistical evaluations, some of the more important ones being:

- 1) The conductance of the deposit is improved by lowering the pH of the  $\text{FeSO}_4$  solution or adding thiourea to the reductant. The optimum values of various parameters appear to be ~5.3 pH 100 gpl AgF, 2 pH saturated  $\text{FeSO}_4$  with 0.5 gpl thiourea for both ivory and enamel substrates.

- 2) The rate of deposition increases with increasing AgF pH (5.3 better than 1.5) or concentration (100 gpl better than 50 gpl), or using thiourea in the reductant (0.5 is the optimum for a range of 0.0 to 1.0 thiourea).
- 3) Morphologically, the grain size of the deposit decreases with the use of thiourea and the optimum concentration appears to be 0.5 gpl when 100 gpl AgF and saturated  $\text{FeSO}_4$  pH are 3.3 and 2.0 respectively for both ivory and enamel substrates. However, at AgF pH's higher than 3.3, the thiourea might have less of an effect in reducing the grain size although other properties such as wear resistance might improve as noted below.
- 4) The wear resistance improves with the use of thiourea and with increasing pH of AgF. The optimum conditions for enamel substrates appear to be ~5.4 pH 100 gpl AgF and 2 pH saturated  $\text{FeSO}_4$  with 0.3 gpl thiourea.
- 5) The shear strength of the amalgamated deposit increases with the use of thiourea. The shear strength of the amalgamated silver deposits obtained from  $\text{FeSO}_4$  approached that of  $\text{N}_2\text{H}_4$  reduced deposits when 0.5 gpl thiourea was used in 2 pH saturated  $\text{FeSO}_4$  solution with 3.8 pH 100 gpl AgF for ivory substrate.

The ascorbic acid as a reducing agent has given very encouraging results to date. Particularly because of the compatibility and non-toxic nature, it is very promising and worth investigating further.

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